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Japanese Published Unexamined (Kokai) Patent Publication No. 59-050190; Publication Date: March 23, 1984; Application No. 57-162757; Application Date: September 17, 1982; Int. Cl.³: C25D 3/56; Inventor: Mitsuaki Atobe; Applicant: Suwa Seikosha Co., Ltd.; Japanese Title: Denkainikkeru Rin Goukin Mekkiyoku (Nickel-Phosphorus Alloy Electroplating Bath)

Specification

1. Title of Invention

Nickel-Phosphorus Alloy Electroplating Bath

2. Claim

A nickel-phosphorus alloy electroplating bath, characterized by being composed of the following components at the following amounts: nickel sulfamate at 100 to 700 g/l; nickel chloride at 0 to 45 g/l; boric acid at 15 to 50 g/l; phosphorus acid at 5 to 100 g/l; phosphoric acid at 5 to 100 g/l; EDTA at 10 to 100 g/l; and sodium lauryl sulfate at 0.01 to 0.5 g/l.

3. Detailed Description of the Invention

This invention pertains to a nickel-phosphorus alloy electroplating bath that is highly corrosion resistant and electrodepositable at a high speed and that produces a mirror surface film.

A conventional nickel-phosphorous alloy electroplating contains a low amount of phosphorus. In particular, the electroplating has a limitation in the use in a field that requires corrosion resistance. If the amount of phosphorous contained increases, the deposition speed rapidly decelerates. The limitation in the amount of phosphorus

contained is also 14 to 15%. For these reasons, the amount of phosphorus contained in a deposit is 12% or less. In addition, tarnish often occurs on the outer appearance. Thus, the conventional electroplating is not suited for high-class accessories. In particular, pits often occur by generation of hydrogen.

The present invention is produced to eliminate the aforementioned disadvantages of the invention. The purpose of the invention is to offer a nickel-phosphorus alloy so as to obtain a film having high corrosion resistance, high electrodeposition performance and a mirror surface.

At a bath, nickel sulfamate that demonstrates high dissolution is used for nickel ions to be a supply source for nickel. The concentration is 100 to 700 g/l, preferably 300 to 500 g/l. If the concentration is 100 g/l or lower, the electrodepositing speed decreases. It is also difficult to add a high current density. Nickel chloride at 0 to 45 g/l is used to dissolve a nickel anode, which is not always required if the nickel anode is not used. Boric acid at 15 to 50 g/l is used as a PH buffering agent. The boric acid is preferably used at 40 to 50 g/l and turns black of a nickel-phosphoric film into white. If the amount of boric acid is 50 g/l or larger, precipitation occurs. Phosphorous acid at 30 to 100 g/l is used as a phosphoric supply source. The phosphorous acid is preferably used at 40 to 70 g/l and can stably obtain a 16 or more % phosphoric contained in the film. In particular, pits are rapidly reduced by adding EDTA at 10 to 100 g/l, preferably 40 to 60 g/l, thereby obtaining a mirror surface luster without having tarnish. When EDTA is added at 100 g/l or larger, the bath becomes instable to sometimes cause precipitation. Furthermore, sodium lauryl sulfate is added at 0.01 to 0.5 g/l as an anti-pit agent, preferably at 0.1 to 0.2 g/l. If sodium lauryl sulfate is added at 0.5 g/l or larger, an excessive foaming occurs,

which is not desirable. Phosphoric acid added at 5 to 100 g/l increases the amount of phosphoric contained. The phosphoric acid is preferably added at 30 to 60 g/l. If the amount of phosphoric acid is added at 100 or larger g/l, acidity is excessively high to damage the article to be plated and also increase the number of pits.

The invention is described hereinbelow with reference to the working examples.

Working Example 1

A pretreatment such as a degreasing is applied to a brass made clock case. A plating at 4 μm is then applied to the clock case at pH 0.8 at a 60°C bathing temperature at a 6 A/dm² current density for 10 minutes by a rotating agitation means in a nickel-phosphorus alloy plating bath that is composed of nickel sulfamate at 450 g/l, boric acid at 45 g/l, phosphorous acid at 40 g/l, phosphoric acid at 40 g/l, EDTA at 30 g/l and sodium lauryl sulfate at 0.1 g/l. After rinsing with water, a rhodium plating is applied at about 0.15 μm by a predetermined means. When a nickel-rhodium plating is applied, electrochemical corrosion usually occurs. Due to the corrosion resistance problem, a noble metal plating such as a palladium plating is applied between the nickel film and the rhodium film. At a nickel-phosphorus alloy plating with a 13 or less % phosphorous contained, satisfactory data cannot also be obtained at an anti-corrosive test using an artificial sweat due to a direct rhodium plating.

When a plating by the invention is applied, the amount of phosphorous contained is 15% or more, which is more sufficient than that when palladium is used at the anti-corrosive test using the artificial seat. Furthermore, a mirror surface without presenting any plating abnormalities such as pits and tarnish is obtained. A value at 4 im/10 minutes

is achieved at this high phosphorous containing state. The adhesiveness is evaluated by a bending test. No problem is found. Excessive luster is controlled on the seam to achieve a high-class texture for a white plating.

Working Example 2

After a pretreatment such as a degreasing has been applied to a kana (material: carbon steel) as a watch ring arrangement component, a flash plating is applied at pH 0.78 at a 65°C bathing temperature at a 0.2 A/dm² current density for one minute using a rotating agitator in a nickel-phosphorus alloy plating bath that is composed of the following components at the following amounts: nickel sulfamate at 400 g/l; boric acid at 45 g/l; phosphorous acid at 50 g/l; phosphoric acid at 50 g/l; EDTA at 40 g/l; and sodium lauryl sulfate at 0.2 g/l. When a nickel plating is applied to carbon steel, the corrosion resistance is usually low. When this nickel-phosphorus film (17% phosphorus contained) is tested by an artificial sweat, corrosion resistance is about 5 times higher than that of prior art plating is demonstrated. It is also evident that the smoothness of kana improves in comparison with the nickel film.

Working Example 3

As for a plating bath composition, nickel sulfamate at 350 g/l, nickel chloride at 30 g/l, boric acid at 45 g/l, phosphorous acid at 50 g/l, phosphoric acid at 40 g/l, sodium lauryl sulfate at 0.05 g/l and EDTA at 20 g/l are used. A plating is applied at a 65°C bathing temperature at a 2 A/dm² current density for 10 minutes using a brass plate as a cathode to obtain a plated article having a mirror-surface luster at a 1.0 μm thickness. The

ratio of phosphorus contained in the film is 16.5%. The corrosion resistance by the artificial sweat, the chemical agent resistance by nitric acid and the adhesiveness by the bending test are sufficient.

Working Example 4

An electric plating is applied at a 60°C bathing temperature at a 4 A/dm² current density using a nickel plate as an anode and a brass watch case as a cathode in a nickel-phosphorus alloy bath (pH 0.8) that is composed of the following components at the following amounts: nickel sulfamate at 450 g/l; nickel chloride at 30 g/l; boric acid at 45 g/l; phosphorous acid at 40 g/l; phosphoric acid at 40 g/l; EDTA at 30 g/l; and sodium lauryl sulfate at 0.1 g/l. A gold plating is further applied at 3 μm by using a regular method. The obtained deposit demonstrates a mirror-surface luster and a reduced luster on the seam, thereby achieving a high-class texture. The corrosion resistance also improves 4 to 5 or more times higher than that of the nickel use. At the time, the thickness of the nickel-phosphorus alloy film is 2 μm. The adhesiveness by the bending test is also sufficient.

As described above, the plating bath by the invention is particularly used for a variety of purposes such as a field that requires corrosion resistance and chemical agent resistance, a field that requires a film for lining a noble metal plating (e.g., decorative components) and the like. Thereby, the invention is useful.

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